

Electron microscopic nanostructure and optical characterization of chemically prepared ZnTe thin film

M Rasmani Devi, Dr. K. Kunjabali Singh

Abstract— Wet Chemical Bath Deposition technique was used to synthesize ZnTe nanocrystals at molar. XRD results showed quantum size nanoparticles in the ZnTe films at different molar concentrations. The surface structures of the films were studied from FESEM micrograph which showed that the agglomeration of ZnTe spherical grains led to the formation of relatively bigger grains of uniform spherical shape of different sizes and extend smoothly the entire surface of the substrates without pinholes. The deposited ZnTe nanocrystals were found zinc blend structure with multifaceted deflection planes with most prominent along (200) plane at lower diffraction angle below 300. The peak intensity were found to increase with increasing Zn²⁺ and Te²⁻ ion concentrations and molar and showed nanocrystalline growth in the film with quantum dot size between 8.31 – 14.9nm. The optical analysis of the ZnTe quantum dots films revealed that the absorption coefficient was found to enhance at lower wavelength at low molarity showing blue shift in lower wavelength spectral side. The absorption coefficients were enhanced at higher wavelength at higher molarity which were the signs of red shifts in higher wavelengths spectral sides and may be attributed due to increase of agglomeration of quantum size nanoparticles under quantum size effect absorbing more photonic energies of lower wavelength as well as higher wavelength with less transitions.

Index Terms— ZnTe thin films, XRD, FESEM, quantum dots, band gap, optical properties.

I. INTRODUCTION

Characterization of thin solid films prepared by several techniques is important for understanding the behaviour of surface roughness, uniformity, crystallinity, carrier mobility, optical and electrical properties etc for different technological applications. ZnTe belongs to II-VI compound inorganic semiconductors with direct bulk energy gap of 2.26eV and is found to be technologically important for different applications viz (i) Photodetectors, (ii) LED, (iii) Solar Cells¹ (iv) Photovoltaic Cells², (iv) Light refractors³. ZnTe has high absorption co-efficient and shows p-type nature⁴. In the present paper, ZnTe nano sized thin films dispersed in polyvinyl alcohol (PVA) were synthesized at different molar concentrations of zinc and tellurium ions sources by simple wet chemical bath deposition (CBD) method at room temperature and investigate their micro structures and optical properties using Field Emission

Scanning Electron Microscope (FESEM), X-ray diffractometer (XRD) and UV-vis-spectrophotometer.

II. EXPERIMENTAL DETAIL

ZnTe nanocrystals were synthesized at different molar 0.1M, 0.2M, 0.4M, 0.6M and 0.8M by wet CBD technique on ultra fine glass substrates using ZnSO₄ (M. Wt. = 287.54gm) as Zn²⁺ - source and Na₂Te (M. Wt.= 221.58gm) as Te²⁻ - ion source at equimolar solutions. For synthesis of 0.1M ZnTe nanocrystals, 2.875gm of ZnSO₄ was dissolved in 80ml of double distilled water and stirred with a magnetic stirrer for 30mins in a 100ml cleaned glass beaker. In another glass beaker, 2.216gm of Na₂Te was also dissolved in 80ml distilled water and stirred for 30mins. Then, 40ml of ZnSO₄ solution was mixed with 80ml of Na₂Te to make ratio of 1:2 and then stirred for half hour at room temperature. A few drops of ammonium hydroxide (NH₄OH) solution was added drop-wise in the precursor to adjust its p^H value at 10. In a third beaker, 2gm of PVA was added in a 100ml double distilled water to make 2wt. % PVA and heated at 50^oC with constant stirring for 30mins. Then 20ml. of 2wt.% PVA was mixed with the above precursor and then heated at 70^oC with constant stirring till the PVA dissolved. When the solution was cooled down to room temperature, the glass substrates (5nos.) were kept immersed vertically in the solution for a week when ZnTe nanoparticles were found deposited on the substrates. The substrates were annealed at 10^oC above room temperature in a closed microwave oven for a night for completely growth of the ZnTe crystal at the molar. The process was repeated for growth of ZnTe thin films at other molar also for which the amount of the materials have been shown in Table-1.

III. RESULTS AND DISCUSSION

3.1. Structural Characterization of ZnTe films

X-ray diffractions of the as deposited ZnTe thin films at different molar concentrations were taken for microstructural characterization as shown in Fig. 1. The surface morphology of the ZnTe films were studied from the FESEM images as shown in Fig.2. The as deposited ZnTe nanocrystals were found to be zinc blend structure with different reflection planes as shown in the low angle X-ray diffraction spectra obtained from Phillips X' pert Pro-Automated Powder X- ray diffractometer (Model APD 1700 with CuK_α- radiations ($\lambda = 1.572\text{\AA}$) available in NIT, Manipur. The lattice parameters of the phase structure of the ZnTe films at different molar concentrations were calculated using the Bragg's relation⁵

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$$2d\sin\theta = n\lambda \quad (1)$$

Whence

$$\sin^2\theta = \frac{\lambda^2 N}{4a^2} \quad (2)$$

where

$$N = h^2 + k^2 + l^2 \quad \text{and} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

The most prominent diffraction plane was found at (200) plane at lower diffraction angle below 30°. The diffraction peak intensity were found to increase with increasing Zn²⁺ and Te²⁻ ion concentrations and molars and showed nanocrystalline growth in the film. The lattice parameters corresponding to the different (hkl) planes and the surface topology of the film have been shown in the **Table -2** below while nanocrystalline particle sizes estimated from the ZnTe films at molars x = 0.2M, 0.4M, 0.6M and 0.8M using the Scherrer's relation given in eqn. (4) at maximum FWHM intensity in ZnTe films and have been shown in the corresponding Table-3

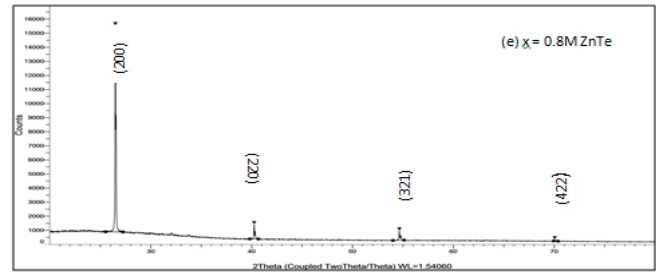


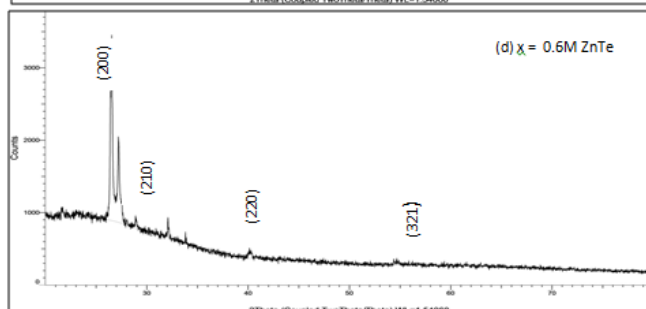
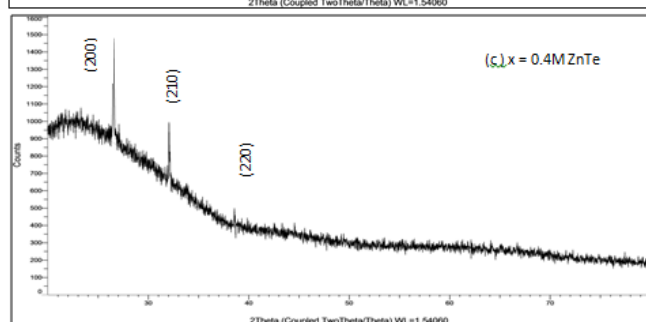
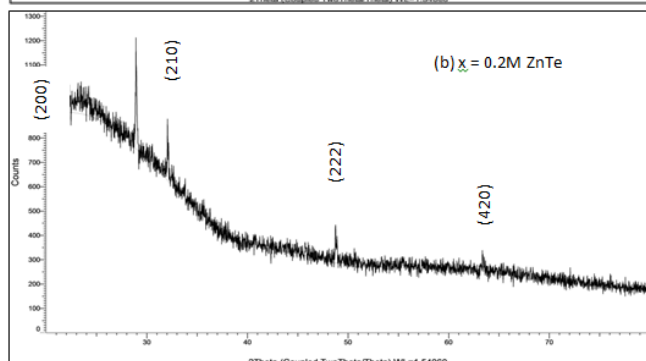
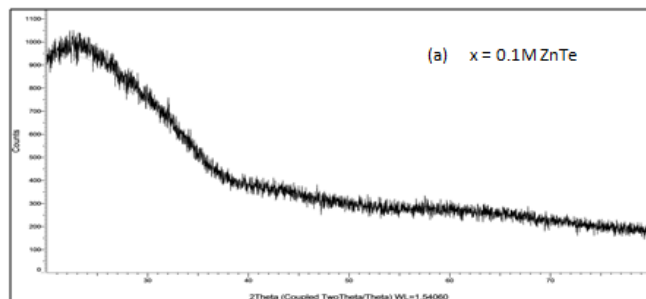
Fig. 1. XRD patterns of molar dependent ZnTe films.

Table- 1. Amount of chemicals for synthesis of ZnTe films at different molarity.

Mol. wt. of ZnSO ₄	Molarity (M)	Quantity of ZnSO ₄ (gm)	Mol. wt. of Na ₂ Te (gm)	Quantity of Na ₂ Te (gm)
287.54	0.1	2.875	221.58	2.216
	0.2	5.751		4.432
	0.4	11.502		8.863
	0.6	17.252		13.295
	0.8	23.003		17.726

Table-2. ZnTe nanocrystal lattice parameters at different molars.

Molar (x)M	I/I ₀	2θ-value (degree)	(hkl) plane	a _{cal.} -value (nm)	d _{cal.} -value (nm)
0.1
0.2	1200	28	200	0.6366	0.3183
	880	32	210	0.6217	0.2734
	450	49	222	0.6432	0.1851
0.4	340	63.5	420	0.6534	0.1461
	1470	26	200	0.6844	0.3422
	1000	32	210	0.6247	0.2794
0.6	500	38.5	220	0.6590	0.2330
	3450	27	200	0.6598	0.3299
	2000	28.5	200	0.6235	0.3118
	950	32	210	0.6247	0.2794
	800	34	211	0.6449	0.2633
0.8	600	40	220	0.6367	0.2251
	500	55	321	0.6240	0.1668
	15500	26.5	200	0.6696	0.3348
	1600	40.5	220	0.6278	0.2220
0.8	1500	54.5	321	0.6282	0.1679
	1000	70	422	0.6576	0.1342



The surface structures of ZnTe films at varied synthesized molars are shown in the FESEM images of the films in Fig.2 under magnification x 100,000. From the micrograph, it was speculated that the agglomeration of spherical grains led to the formation of relatively bigger grains of uniform spherical shape of different sizes and extend the entire surface of the substrates without pinholes. The average grain sizes were calculated from Scherrer relation⁶

$$d_{hkl} = \frac{\lambda K}{\beta \cos\theta} \quad (4)$$

where λ is wavelength of X-rays, the value of shape factor K is 0.94, β the full-width half maximum intensity and θ is the corresponding diffraction angles. The calculated values of particle diameter were found between 10 – 15nm ranges Table - 3.

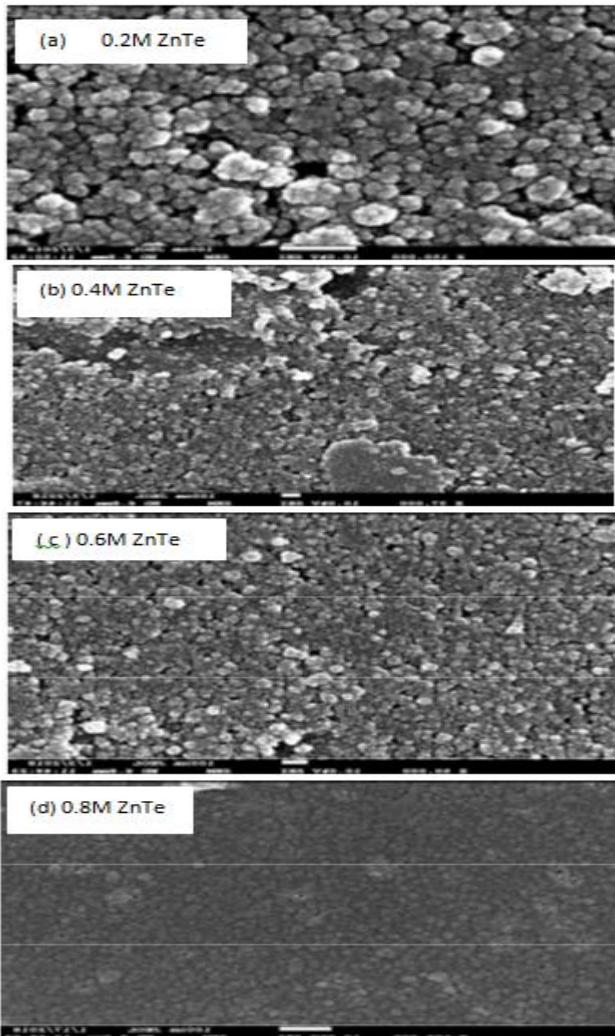


Fig.2. FESEM images of ZnTe films at molar

Table-3. Particle sizes determined from XRD spectra of ZnTe films

Molarity x (M)	I/I ₀	(hkl)-value	2θ ₁ -value (degree)	2θ ₂ -value (degree)	d _{hkl} -value (nm)
0.1
0.2	1200	200	28	29	14.9
0.4	1470	200	26	27	14.9
0.6	3450	200	26	28	8.31
0.8	15500	200	26	27	14.9

The dislocation density in the films was calculated from the Willamson and Smallman's relation⁷

$$\delta = \frac{1}{D^2} \quad (5)$$

The chemically deposited ZnTe nanocrystalline thin films grown under suitable experimental conditions contain a large number of localized microstrains (ε) due to thermal effects and film thickness and has greater influence in the photo-electrical transport properties in the films (). The microstrains were calculated from the relation⁸

$$\epsilon = \beta \frac{\cot \theta}{4} \quad (6)$$

where β is FWHM in radian and θ diffraction angle at the full width maximum intensity. The values of dislocation density and microstrains have been shown in table-4.

Table-4.

Sample	FWHM B (radian)	Grain size D (nm)	Dislocation density (δ)	Microstrain (ε)
0.2M ZnTe	8.73 x 10 ⁻³	14.9	4.504 x 10 ⁻³	25 x 10 ⁻²
0.4M ZnTe	8.73 x 10 ⁻³	14.9	4.504 x 10 ⁻³	25 x 10 ⁻²
0.6M ZnTe	1.746 x 10 ⁻³	8.31	1.448 x 10 ⁻²	24.99 x 10 ⁻²
0.8M ZnTe	8.73 x 10 ⁻³	14.9	4.504 x 10 ⁻³	25 x 10 ⁻²

The estimated particle sizes indicate that ZnTe nanoparticle lie in quantum dot ranges. The as grown ZnTe films are observed to contain fairly uniform dislocation density and microstrains which are not affected by the changing molar concentrations in the films.

3.2. Optical properties in ZnTe films

Optical absorption in the visible wavelengths range were studied in view of technological applications using UV-vis spectrometer (model : Lamda 35LS 35, Parkin Elimer 2008). The Fig.3 shows the absorption vs. wavelength curves of ZnTe films at different molar. The optical absorption co-efficient α in the films is co-related to the photon energy as

$$\alpha = A \frac{(\hbar\nu - E_g)^{n/2}}{\hbar\nu} \quad (7)$$

where E_g is the band gap energy, A constant being different for different transitions and n a constant being equal to 1 for direct band gap semiconductor.

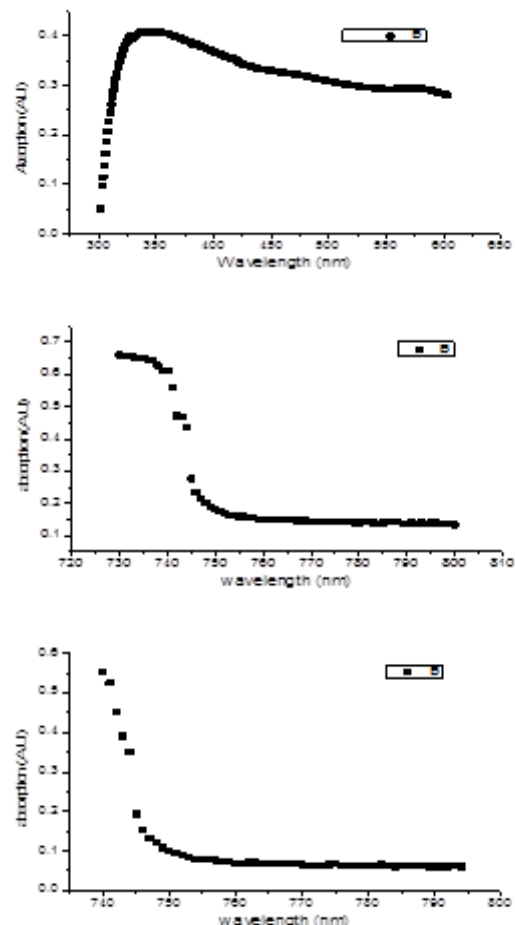


Fig.3. Absorption vs. wavelength curve of ZnTe film at (a) x

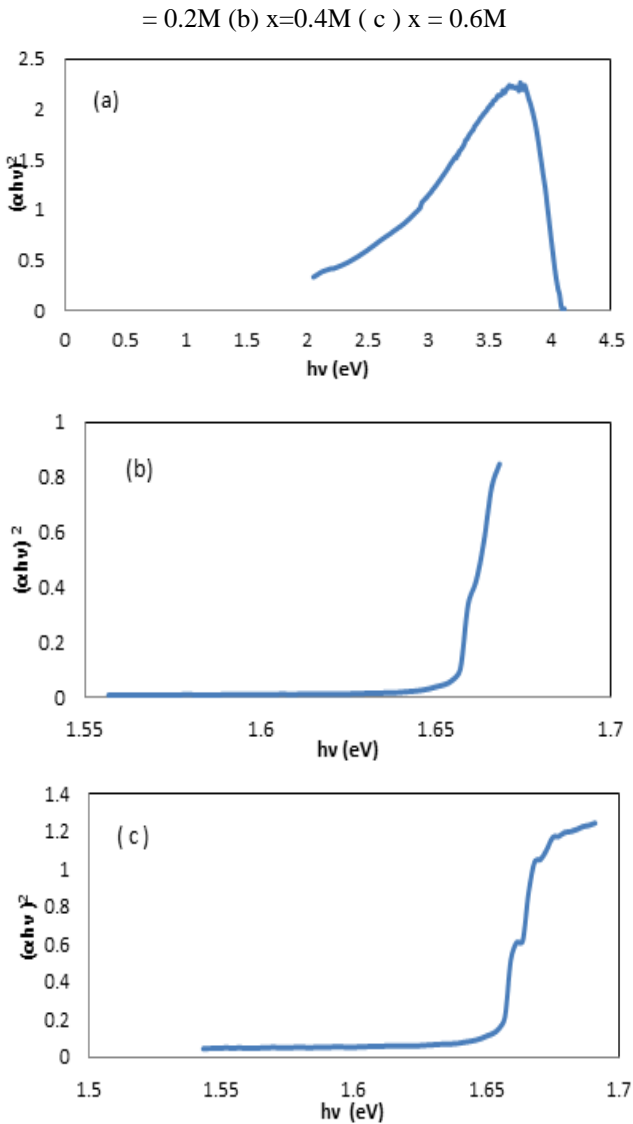


Fig. 4. $h\nu$ vs. $(\alpha h\nu)^2$ curves of ZnTe films at (a) 0.2M, (b) 0.4M and (c) 0.6M

Table-4 Energy band gaps in fresh ZnTe nanocrystalline films

Molarity (M)	Energy band gap (eV)	Particle diameter (nm)
0.2	1.9	14.9
0.4	1.66	14.9
0.6	1.67	8.31

The optical analysis of the ZnTe quantum dots films reveal that the absorption coefficient, α is found to enhance at lower wavelength at low molarity showing blue shift in lower wavelength spectral side. The absorption coefficients are found enhanced at higher wavelength at higher molarity which are the signs of red shifts in higher wavelengths spectral sides and may be attributed due to increase of agglomeration of quantum size nanoparticles under quantum size effect absorbing more photonic energies of lower wavelength as well as higher wavelength with less transitions. The energy band gaps in the films were found decreased than that of bulk value due to quantum size effects.

IV. CONCLUSION

As deposited ZnTe nanocrystals were found to be zinc blend structure with different reflection planes with most prominent diffraction plane along (200) plane at lower diffraction angle below 30° . The diffraction peak intensity were found to increase with increasing Zn^{2+} and Te^{2-} ion concentrations and molar and showed nanocrystalline growth in the film with quantum dot size particle diameters between 8.31 – 14.9nm. From the FESEM micrograph, it was speculated that the agglomeration of spherical grains led to the formation of relatively bigger grains of uniform spherical shape of different sizes and extend the entire surface of the substrates without pinholes. The average grain sizes were found 10 – 15nm ranges. The experimental values of the particle sizes reveal that as deposited ZnTe films at different molarity were approaching of quantum dot sized nanoparticles. The optical analysis reveals that the absorption coefficient is enhanced at lower wavelength at low molarity showing blue shift in lower wavelength spectral side. The absorption coefficients are found enhanced at higher wavelength at higher molarity which are the signs of red shifts in higher wavelengths spectral sides and may be attributed due to increase of agglomeration of quantum size nanoparticles under quantum size effect absorbing more photonic energies of lower wavelength as well as higher wavelength with less transitions. It is observed that the band gap decrease with reduction in particle sizes. Some fairly uniform dislocation density and microstrains were observed which are not affected by the changing molar concentrations in the films.

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